UNIVERSITI PUTRA MALAYSIA

IMPROVING LIQUID FERTILIZER UREA EFFICIENCY USING HUMIC ACIDS ADDITIVES EXTRACTED FROM TROPICAL PEAT

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FP 2009 1

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By

SUSILAWATI BINTI KASIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Doctor of Philosophy

June 2009

DEDICATION

Dedicated to all people who have contributed their brilliant ideas, wisdom words and efforts to finish this thesis. It is also dedicated to those who have helped me along my way, during my hard time in finishing my study.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirements for the degree of Doctor of Philosophy

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June, 2009

Chairman : Osumanu Haruna Ahmed, PhD

Faculty : Faculty of Agriculture and Food Sciences

One of the most important sources of organic matter is peat. Being organic in nature, peat are high in humic and fulvic acids. These substances can be reconstituted with N and K to produce ammonium and potassium-humates (organic fertilizer). This could be realized if they could be rapidly and cheaply isolated from peat soils. Factors which affect the humic and fulvic acids isolation from soils include extraction, fractionation, and purification periods. Thus, part of this study investigated whether a relationship could be separately established between extraction time, fractionation time, and the yield of humic acids (HA) of tropical peat soil (hemists), as well as the relationship between both variables on the yield of HA of this soil. Modified standard procedures using 0.1 M KOH (analytical grade) were used to isolate humic acids from the soil. Results showed that, there was a quadratic relationship between extraction period and yield of HA. There was however no relationship between fractionation period and yield of HA. There was negative correlation between the yields of extraction and fractionation periods. This finding enables the isolation of HA of hemists in less than 10 h instead of existing average period of 2 to 7 days, therefore helping in facilitating the idea of producing for instance ammonium-humate or potassium-humate (N and K foliar organic fertilizers) from peat. The second part of the study was development of NH_4^+-K-humate by reconstitution of humic and fulvic acids. The organic fertilizers developed via reconstitution were evaluated under laboratory conditions. Effectiveness of organic fertilizer in enhancing N availability was the main concern of this study. This was due to high N loss by N fertilizer (e.g. urea) after surface application. Nine treatments namely urea (solid), urea (liquid), ammonium sulfate (solid), ammonium sulfate (liquid), humic acids + urea, fulvic acids + urea, humic and fulvic acids (acidified) + urea and humic, fulvic acids (unacidified) + urea and control (soil alone) were used in this study with the aim of reducing N loss from urea application. A closed dynamic air flow system was used to estimate N loss from soil. Usage of fulvic together with urea decreased soil pH and as well as ammonia volatilization. However, the use of HA significantly reduced ammonia volatilization. This suggests the effectiveness of the organic based fertilizer formulated in controlling N loss and enhancing N availability. Besides being effective in controlling N loss, promotion of plant growth and development are other factors which should be considered in order to confirm the effectiveness of the formulated organic fertilizer. Hence, a pot experiment (third part of the study) was set up with seven treatments excluding liquid ammonium sulfate. Results showed that, organic based N fertilizers enhanced N, P and K uptake. They also promoted N use efficiency particularly for the treatments with fulvic acids. Thus, the formulated fertilizers

(organic fertilizers) have the potential to serve as an alternative fertilizer in reducing N loss, enhancing nutrient uptake and N use efficiency.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENAMBAHBAIKAN KEBERKESANAN BAJA CECAIR UREA DENGAN MENGGUNAKAN ADITIF ASID HUMIK YANG DIEKSTRAK DARIPADA TANAH GAMBUT TROPIKA

Oleh

SUSILAWATI BINTI KASIM

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Salah satu sumber bahan organik yang penting adalah gambut. Ianya adalah organik secara naturalnya dan tinggi kandungan asid humik dan fulvik. Kedua-dua asid ini boleh digabungkan dengan N dan K untuk menghasilkan amonium dan potasium-humate yang boleh dikategorikan sebagai baja organik. Ianya adalah lebih baik jika asid humik dan fulvik dapat diisolasi dengan lebih cepat dan murah daripada tanah gambut. Beberapa faktor mempengaruhi isolasi asid humik dan fulvik ini seperti jangkamasa pengekstrakan, penyisihan dan penulenan. Maka, sebahagian daripada kajian ini adalah meneliti samada terdapat perhubungan yang berasingan antara masa pengekstrakan dan masa penyisihan dengan asid humik yang dihasilkan daripada tanah gambut tropika (*hemists*). Begitu juga perkaitan di antara kedua-dua faktor tadi dengan asid humik yang dihasilkan. Kaedah piawai yang telah diubahsuai yang menggunakan 0.1 M KOH (gred analitikal) telah digunakan dalam mengisolasi asid humik daripada tanah. Keputusan menunjukkan terdapat perhubungan

kuadratik di antara jangkamasa pengekstrakan dengan asid humik yang dihasilkan. Manakala tidak ada perhubungan yang dapat diberikan antara jangkamasa penyisihan dan asid humik yang dihasilkan. Asid humik yang dihasilkan dairpada jangkamasa pengekstrakan dan penyisihan yang berbeza telah memberikan korelasi yang negatif. Penemuan daripada kajian ini mendapati bahawa pengisolasian asid humik daripada hemists dapat dilakukan dalam jangkamasa 10 jam berbanding jangkamasa purata yang ada kini dari 2 ke 7 hari. Maka ianya telah menyumbang kepada idea baru dalam penghasilan baja amonium-humate dan potasium-humate sebagai baja organik dalam bentuk cecair daripada tanah gambut. Bahagian kedua kajian ini adalah penghasilan baja organik daripada penyusunan semula asid humik dan fulvik. Baja yang terhasil daripada penyusunan semula asid humik dan fulvik ini akan diuji dalam makmal. Keberkesanan baja organik dalam meningkatkan kedapatan N adalah matlamat utama kajian ini. Ini adalah kerana, kehilangan N yang tinggi telah didapati daripada baja urea yang diberikan dipermukaan tanah. Sembilan rawatan baja [yang terdiri daripada urea (pepejal), urea (cecair), ammonium sulfat (pepejal), amonium sulfat (cecair), asid humik + urea, asid fulvik + urea, asid humik dan fulvik (diasidkan) + urea, asid humik dan fulvik (yang tidak diasidkan) + urea, dan tanah (tanpa apa-apa rawatan baja)] telah digunakan dengan matlamat untuk mengurangkan kehilangan N daripada penggunaan baja urea. Sistem aliran udara tertutup telah digunakan dalam menganggar kehilangan N daripada tanah. Penggunaan asid fulvik bersama-sama dengan urea telah mengurangkan peningkatan pH tanah begitu juga dengan pemeruapan amonia. Manakala penggunaan asid humik telah mengurangkan pemeruapan amonia dengan signifikan. Hasil dari kajian ini telah menunjukkan bahawa keberkesanan baja cecair organik N yang telah diformulasi dalam mengurangkan kehilangan N dan seterusnya mengurangkan masalah pencemaran alam sekitar. Di samping dapat mengurangkan kehilangan N dengan baik, galakan kepada pertumbuhan dan tumbesaran pokok adalah faktor lain yang patut diberikan perhatian bagi memastikan keberkesanan baja yang telah dihasilkan. Maka, kajian di rumah kaca (bahagian ketiga kajian) dengan menggunakan pasu telah dibuat dengan menggunakan tujuh rawatan baja tidak termasuk amonium sulfat. Keputusan menunjukkan bahawa baja organik N dapat meningkatkan pengambilan nutrien (N,P dan K). Ianya juga berjaya menggalakkan keberkesanan penggunaan baja N terutamanya rawatan yang menggunakan asid fulvik. Maka baja yang diformulasi iaitu baja organik mempunyai potensi untuk bertindak sebagai baja alternatif dalam mengurangkan kehilangan N, mempertingkatkan pengambilan nutrien dan menggalakkan keberkesanan penggunaan baja N.

ACKNOWLEDGEMENTS

All praises are for Allah, the Exalted, Merciful and Magnificent. Many thanks and gratefulness go only to Allah for the strength given to me to deal with the trials and tribulations during my study. This trying moment could not be endured without Allah.

Special thanks also go to my supervisory committee namely Dr. Osumanu Haruna Ahmed (Chairman), Prof. Dato' Dr. Nik Muhamad Ab. Majid (member) and Prof. Dr. Mohd Khanif Yusop (member), for their support, encouragement, and constructive comments and suggestions during this research.

I sincerely thank my family members especially my dearest mother, Zaiton for her understanding and patience. Lastly, a big thank you to all of the technical staffs of the Soil Science Laboratory at Universiti Putra Malaysia Bintulu Campus, Sarawak, Malaysia for their assistance and help. A special thank you also goes to all of my dear friends, who consistently encouraged me to pursue my dream.

I certify that a Thesis Examination Committee has met on 10 Jun 2009 to conduct the final examination of Susilawati binti Kasim on her thesis entitled "Improving Liquid Fertilizer Urea Efficiency Using Humic Acid Additives Extracted from Tropical Peat" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirements for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

SUSILAWATI BINTI KASIM

Date : 7 July 2009

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

NH_4^+	Ammonium ion
NO_3	Nitrate
N	Nitrogen
P	Phosphorus
K	Potassium
Mn	Manganese
Zn	Zinc
CEC	Cation Exchange capacity
USA	United State of America
C	Carbon
HA	Humic Acids
FA	Fulvic Acids
PFP	Partial factor productivity
AE	Agronomic efficiency
RE	Recovery efficiency
PE	Physiology efficiency
Fe	Ferrum
Cu	Copper
B	Boron
S	Sulphur
K^+	Potassium ion
Mg	Magnesium
Ca	Calcium
SOM	Soil organic matter
NMR	Nuclear magnetic resonance
DOC	Dissolved organic carbon
Al	Aluminium
OH	Hydroxyl group
COOH	Carboxyl group
EC	Electrical conductivity
USDA	United State Department of Agriculture
FAO	Food and Agriculture Organization
UNESCO	United Nations Educational, Scientific, and Cultural Organization
H	Hydrogen
O	Oxygen
MHA	Mobile humic acids
CaHA	Calcium humic acids
ß-HA	Beta humic acids
α-HA	Alpha humic acids
HCl	Hydrochloric acid
HF	Hydrogen fluoride
NaOH	Sodium hydroxide
N_2	Nitrogen gas

Na	Sodium
$ZnSO_4$	Zinc Sulphate
HS	Humic substances
NH_4NO_3	Ammonium nitrate
EU	European Nation
NH_3	Ammonia
NO	Nitric oxide
N_2O	Nitrous oxide
PAN	Potential available nitrogen
NBPT	N-(n-butyl) thiophosphoric triamide
TSP	Triple superhosphate
PG	phosphogypsum
DAP	Diammonium phosphate
NH_4Cl	Ammonium cloride
KCl	Potassium cloride
$CaCO_3$	Calcium carbonate
FC	Field capacity
NH_4AOc	Ammonium acetate
g	gram
H_2SO_4	Sulfuric acid
MgO	Magnesium oxide
KOH	Potassium hydroxide
AAS	Atomic absorption spectrophotometry
mg	milligram
$NaHCO_3$	Sodium hydrogen carbonate
HNO_3	Nitric acid
ppm	Part per million
ha	hectare
SAS	Statistical analysis system
DNMRT	Duncan's new multiple range test
LHA	Liquid humic acids
LFA	Liquid fulvic acids

CHAPTER 1

INTRODUCTION

Use of organic materials in enhancing soil fertility has been practiced for many years. Organic substances affect soil fertility by supplying minerals, improving soil structure, increasing soil microbial population, increasing cation exchange capacity (CEC) and buffering capacity of the soil. Additionally, they supply humic molecules which serve as macro and micronutrients carrier (Chen *et al.*, 2004; Olsen, 1986; Pilus Zambi *et al.*, 1982). Humic substances also directly affect plant growth and development by promoting various biochemical processes like photosynthesis and nucleic acid synthesis (Chen *et al.*, 2004; Nardi *et al.,* 2002; Young and Chen, 1997).

Enhancing macro and micro-nutrients availability in soil was a credit given by the use of humic substances. Increase of plant growth due to increase of nutrients uptake was commonly pronounced when humic substances are applied to the soil (Varanini and Pinton, 2001; Clapp *et al.*, 2001; Chen and Aviad, 1990). Since ions uptake depends on nutrient concentrations and the medium pH, the use of humic substances could be one of the appropriate approaches in enhancing nutrient availability and uptake in soil (Nardi *et al.,* 2002; Nardi *et al.,* 1991; Maggioni *et al.,* 1987).

As reported in previous studies, use of humic acid (HA) increased the uptake of macro and micro-nutrients of maize plant (Vaughan and Malcolm, 1985; Mylonas and McCants, 1980; Tan and Nopamornbodi, 1979). Organically bound form of micronutrients cations are more available to plants compared to inorganic forms of pools of insoluble inorganic precipitates and those held in primary minerals (Varanini and Pinton, 2006; Mandal and Mandal, 1986; Murthy, 1982). Thus, this approach was practical in boosting nutrients in soil.

Carbon is the other important element in promising healthy and good plant growth. Carbon in the form of soil organic matter can acts as a pool in sustaining soil fertility (Grigal and Ohmann, 1992). It also can improve water holding capacity and nutrient availability in soil (Lal *et al.,* 1998). Since peat can store high amounts of C, it could be a good source for formulating organic based fertilizers (Sorenson, 1993). As reported by Maltby and Immirzi (1993), tropical peats have more than 70 Gt carbon from an area ranging from 33 to 49 Mha. Thus it can be explored carefully and sustainably to formulate better fertilizer. Due to high CEC, acidic nature, water retention capability, and chelation characteristics, peats are suitable medium for organic fertilizer production (Tan, 2003; Stevenson, 1994).

Food production for the increasing world population also requires the development and application of new technologies to produce more food per unit